(11)

EP 0 805 476 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication: 05.11.1997 Bulletin 1997/45

(51) Int Cl.6: **H01J 37/32**

(21) Application number: 97302893.9

(22) Date of filing: 28.04.1997

(84) Designated Contracting States:

BE CH DE DK FI FR GB IT LI NL SE

(30) Priority: 01.05.1996 US 640460

(71) Applicant: THE BOC GROUP, INC.
Murray Hill, New Providence,
New Jersey 07974-2082 (US)

(72) Inventors:

Rietzel, James, G.
 Antoch, California 94509 (US)

Woolley, Christopher, P.
 Martinez, California 94553 (US)

(74) Representative: Bousfield, Roger James et al The BOC Group plc Chertsey Road Windlesham Surrey GU20 6HJ (GB)

(54) Plasma enhanced chemical vapour deposition processes and apparatus

(57) A plasma treating apparatus comprising:

an evacuable chamber (14);

a power source (20) connected to two electrodes in the evacuable chamber (14) so that a plasma can be formed for the treatment of a substrate (22) when it is placed in the evacuable chamber (14);

a gas supply (17) supplying gases for the plasma to a gas injector (12), the gas injector (12) including gas ports (42) for allowing gases to enter the evacuable chamber(14), wherein the gas ports (42) include plugs (40) made of a dielectric material, the plugs having a centre hole (40a) through which the gases pass into the evacuable chamber (14), the plugs (40) fitted securely into the gas injector (12) so that gas does not leak around the sides of the plug (40) into the evacuable chamber (14).

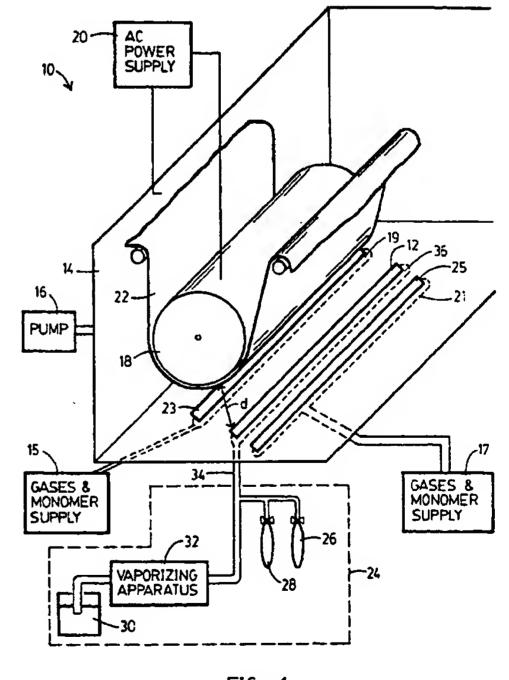


FIG._1.

Description

This invention relates to a plasma-enhanced chemical vapour deposition process and apparatus therefor, especially the plasma-enhanced chemical vapour deposition process used to treat a web rolled through an evacuated chamber.

An example of such a process is described in US Patent No. 5,224,441, the contents of which are incorporated herein by reference. In this patent, gases, including a monomer, for example organosilicon, oxygen, and inert gas, for example helium, are introduced into the evacuated chamber. A glow discharge plasma is formed between two electrodes powered by an alternating current (AC) power supply. A web substrate flows over a drum electrode and is treated by the plasma so that a silicon oxide layer forms onto the web.

It is desired to run a plasma-enhanced chemical vapour deposition process at high currents to allow the substrate to be treated at high speeds, thereby increasing productivity. The use of high currents can cause wrinkling or other damage to the web substrate.

The present invention is concerned with means to avoid these problems in plasma enhanced chemical vapour deposition processes.

In accordance with the invention, there is provided a plasma treating apparatus comprising:

an evacuable chamber;

a power source connected to two electrodes in the evacuable chamber so that a plasma can be formed for the treatment of a substrate when it is placed in the evacuable chamber;

a gas supply supplying gases for the plasma to a gas injector, the gas injector including gas ports for allowing gases to enter the evacuable chamber, wherein the gas ports include plugs made of a dielectric material, the plugs having a centre hole through which the gases pass into the evacuable chamber, the plugs fitted securely into the gas injector so that gas does not leak around the sides of the plug into the evacuable chamber.

It has been found in general that when gases for the process are injected through a typical gas injector at high currents of greater than about 45 amps, the gases can ignite into a plasma jet as soon as they enter the chamber. This ignited plasma can sometimes flow back into the gas supply, causing the early dissociation of the gases. This can cause a reduction in the quality in the deposited layer. Additionally, it was found that a plasma torch formed at the gas inlets can cause the sputtering of the metal material around the port, and thus erode the gas injection hole larger. Finally, it was found that the plasma jet from the gas injector sometimes contacted the web and caused wrinkling of the web and other heat damage.

It was also found that this problem with the high current plasma enhanced deposition process can be avoided by the use of an improved gas injector having dielectric material around the gas outlet port. The use of dielectric material prevents a hollow anode effect from occurring at the gas injector. This prevents the gas from forming a plasma jet at the gas injector port. Additionally, the dielectric material eliminates the sputtering at the port.

In a preferred embodiment of the invention, plugs made of a dielectric material are fitted into ports at the gas injector. These dielectric plugs have a centre hole through which the gases are introduced into the evacuated chamber. The dielectric plugs fit securely into the ports of the gas injector so that the gases cannot flow around the plugs' edges. Plugs made of dielectric material are relatively inexpensive, removable in the case of irreparable damage, and changeable for plugs with a different-sized centre hole if required for a different process.

Plugs without centre holes can be used at some of the locations. This will effectively change the spacing of the gas supply holes which may be beneficial for certain processes.

The use of dielectric plugs also allows for metal material to be used for the remainder of the gas injector. The metal material is cheap compared to the dielectric material, and will also not be brittle like some ceramic materials.

Additionally, the centre hole of the dielectric plugs are preferably less than 0.065 inches in diameter. In a preferred embodiment, the centre hole is about 40 mil in diameter. This size of a hole prevents a plasma from flowing back through the port into the gas manifold. The gas injector can also be electrically isolated from the AC power supply. This also helps avoid the gases from forming a plasma jet as they enter the evacuated chamber.

The above steps help avoid a plasma jet from being formed. Additionally, by angling the gas supply ports so that they flow the gases out away from the web or drum, if a plasma torch is formed at the gas supply, it does not cause heat damage to the web. Additionally, a faceplate can be used to cover the centre holes in the direction between the drum with the web and the holes. The faceplate allows repair personnel to walk on the gas injector without worrying about damaging or clogging the centre holes of the gas injector.

Alternatively, the entire gas injector can be coated or made of a dielectric material to prevent the gases from torching up at the gas injector.

2

20

5

10

15

25

35

30

45

40

50

55

The invention also involves a method of treating a substrate including forming a plasma in an evacuable chamber, supplying gases for the plasma into an evacuable chamber through the gas injector, the gas injector having gas ports including plugs made of a dielectric material, the plugs having a centre hole through which the gases enter into the evacuable chamber. The gas supplying step is such that the gas does not leak around the sides of the plug into the evacuable chamber. The method including the step of placing a substrate into the evacuable chamber and treating it with the plasma.

For a better understanding of the invention, reference will now be made, by way of exemplification only, to the accompanying drawings, in which:

Figure 1 is a diagram of a plasma enhanced chemical vapour deposition system showing the position of the gas injector of the invention.

Figure 2 is a cross-sectional view of the gas injector of the invention.

5

10

15

20

25

30

35

40

45

50

55

With reference to the drawings, Figure 1 is a diagram of a plasma enhanced vapour deposition system 10 showing the position of the gas injector 12. The plasma enhanced vapour deposition system 10 includes an evacuable chamber 14. A pump 16 is used to maintain the gas pressure within the evacuable chamber 14 at the desired level. A drum 18 is used as one of the electrodes of the system, and is attached to an AC power supply 20, for example an AC power supply from Advanced Energy.

A web substrate material 22 flows around the drum 18, which rotates so that a new section of the web 22 can be treated as the web rolls by. A plasma is formed around the drum 18 to treat the web. In a preferred embodiment, a silicon oxide (SiOx) coating is formed on the web material. The plasma causes the dissociation of the monomer material and helps remove impurities from the web coating.

Not shown in this drawing are magnets and baffles which can be used to arrange the plasma around the web material 22. A gas supply 24 is used to supply gas to the plasma enhanced chemical vapour deposition system 10. This gas supply 24, in a preferred embodiment, includes a noble gas supply 26 which can be used to supply helium, an oxygen supply 28, a supply of the liquid monomer 30, and a vaporising apparatus 32. A heated stainless steel (SST) line 34 is used to supply the gases to a manifold 36 shown in phantom below the evacuated chamber 14.

The manifold 36 holds the gases until they flow into the evacuated chamber 14 through the gas injector 12. The details of the gas injector 12 are best shown in Figure 2. Looking again at Figure 1, in a preferred embodiment, there are two additional gas and monomer supplies 15 and 17, two additional manifolds 19 and 21, and two additional gas injectors 23 and 25. Thus, a total of three gas and monomer supply zones are provided in the chamber.

Figure 2 is a cross-sectional view of the gas injector 12' of the invention. In a preferred embodiment, dielectric plugs 40 are used. The dielectric plugs 40 include a centre hole 40a, which preferably has a diameter of less than about 0.065 inches. In a preferred embodiment, the diameter of the centre hole is about 40 mils. The small diameter of the centre hole 40a prevents any plasma from moving back through into the gas manifold and causing premature dissociation of the gases. In a preferred embodiment, the dielectric plug 40 is made of a "fluorogold" material. "Fluorogold" is a ceramic/Teflon (Trade Mark) alloy available from FURON. This material is easy to work but is more expensive than aluminium or other common metals. For this reason, it is less expensive to form only the plugs out of the "fluorogold" material rather than the entire gas injector. It is important that the dielectric plugs are securely fashioned into the port 42 so that no gases leak around the edges of the dielectric plugs. The plugs are preferably 1/16 NPT "fluorogold" pipe plugs with Allen head inserts and 40 mil holes drilled through them. In a preferred embodiment, the plugs are positioned about 1 per inch along the gas injector.

The gas plugs 40 can be easily removed in case of clogging or other damage, and a replacement plug fitted into the gas port. Additionally, if the process is to be changed such that another size centre hole is required, alternate dielectric plugs can be fitted into the gas injector. In a preferred embodiment, the main metal piece 44 of the gas injector 12' is made of aluminium. Aluminium is light, inexpensive, and provides good support for the gas injector. If the gas injector is made of a conductive material, the gas injector should be electrically isolated from the chamber by the use of a dielectric materials located at 100 and 46. A silicon rubber gasket 46 also prevents the gases from leaking around the edges of the gas injector into the evacuated chamber. The gas injector 44 can be screwed down onto the evacuated chamber through the screw holes 48. Screws with a dielectric coating or shell can be used to help maintain the electrical isolation of the gas injector 12' from the chamber. A dielectric shell is preferred because coatings can be chipped or pulled off.

The electrical isolation of the chamber from the gas injector 12' is especially important when the chamber walls are being used as one of the electrodes of the AC plasma system. Maintaining the electrical isolation of the gas injector 12' can help avoid the plasma torch from forming right as the gases are injected into the evacuable chamber. Note that, in the preferred embodiment, the holes 40a in the dielectric plugs 40 are arranged at a 45° angle. By angling the gas as it is injected into the evacuable chamber away from the web or drum, if a plasma torch is formed from the gases as they enter the evacuable chamber, they will not contact the web or drum. Looking at Figure 1, this is relevant because the distance, d, between the drum 18 and the gas injector 12 is about one and one-half inches in a preferred embodiment.

A faceplate 50 is attached to the metal piece 44. The faceplate 50 extends between the ports 48 and the drum electrode so as to prevent dielectric material produced by the system from clogging the holes. In preferred embodiments, the faceplate 50 is partially isolated from the metal piece 44 by a dielectric material, such as an aluminium oxide tape 52. Screws 54 with a dielectric coating 56 are used to connect the faceplate 50 with the metal piece 44. The faceplate 50 also allows for people to walk on top of the gas injector without clogging the holes in the dielectric plugs.

In a preferred embodiment, the gas injector 12' is four inches wide, one inch tall, and 71 inches long. In this preferred embodiment, sixty-six pairs of dielectric plugs with centre holes of forty mil in diameter are provided.

Alternatively, the entire gas injector can be made of a dielectric material or of a material which is coated by a dielectric material. This alternative is more expensive and, if the gas injector were to be made of a ceramic material, it could have problems due to the brittleness of the material.

An example of a process used with the system of Figure 1 is given below.

Gas	Zone No1	Zone No2	Zone No3	Total	
monomer	1.0 slm	1.6 slm	1.0 slm	3.6 slm	
oxygen	3.0 slm	4.0 slm	3.0 slm	10.0 slm	
helium	3.0 slm	4.0 slm	3.0 slm	10.0 słm	

The table gives the gas supply values. The three zones are the gas and monomer supply zones defined by the three gas injectors. The power is about 30.0 KW, current is about 58.0 amps, and voltage at about 515 volts RMS. The web speed is about 100m/min and the deposition rate about 133 angstroms per second.

Claims

10

15

20

25

30

35

1. A plasma treating apparatus comprising

an evacuable chamber (14);

a power source (20) connected to two electrodes in the evacuable chamber (14) so that a plasma can be formed for the treatment of a substrate (22) when it is placed in the evacuable chamber (14);

a gas supply (17) supplying gases for the plasma to a gas injector (12), the gas injector (12) including gas ports (42) for allowing gases to enter the evacuable chamber(14), wherein the gas ports (42) include plugs (40) made of a dielectric material, the plugs having a centre hole (40a) through which the gases pass into the evacuable chamber (14), the plugs (40) fitted securely into the gas injector (12) so that gas does not leak around the sides of the plug (40) into the evacuable chamber (14).

- 2. Apparatus according to Claim 1 in which the dielectric plugs (40) are removable for replacement.
 - 3. Apparatus according to Claim 1 or Claim 2 in which the gas injector (40) is electrically isolated from the power source (20).
- 45 4. Apparatus according to any preceding claim in which the size of the centre hole (40a) is less than 0.065 inches.
 - 5. Apparatus according to any preceding claim in which the gas injector (12) is part of the evacuable chamber (14).
- 6. Apparatus according to any preceding claim in which the gas injector (12) is such that the centre hole (40a) of the plugs (40) is angled away from the closest position of the substrate (22) in the evacuable chamber (14).
 - 7. Apparatus according to any preceding claim in which the gas injector (12) includes a faceplate (50) positioned over the centre holes (40a) in the plugs (40) to prevent the damaging of these centre holes (40a).
- 8. Apparatus according to Claim 7 in which the faceplate (50) is solid enough to support people walking on it during servicing of the apparatus.
 - 9. Apparatus according to any preceding claim in which the power supply (20) is an alternating current power supply.

	 Apparatus according to any preceding claim in which the gas injector (12) is made of a metal material ex the plugs (40). 							
5								
10								
15								
20								
25								
30								
35								
40								
45								
50								
55								

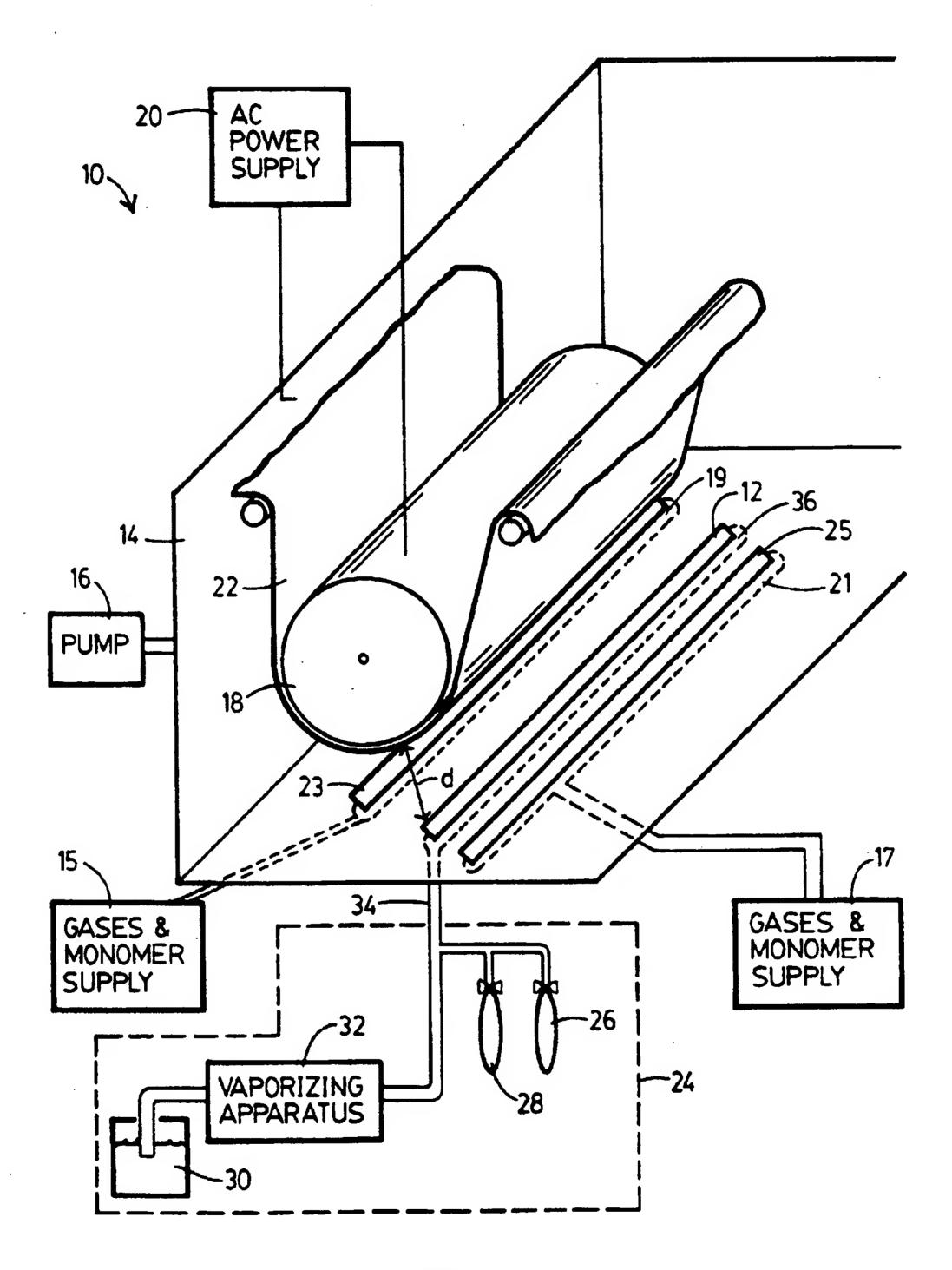
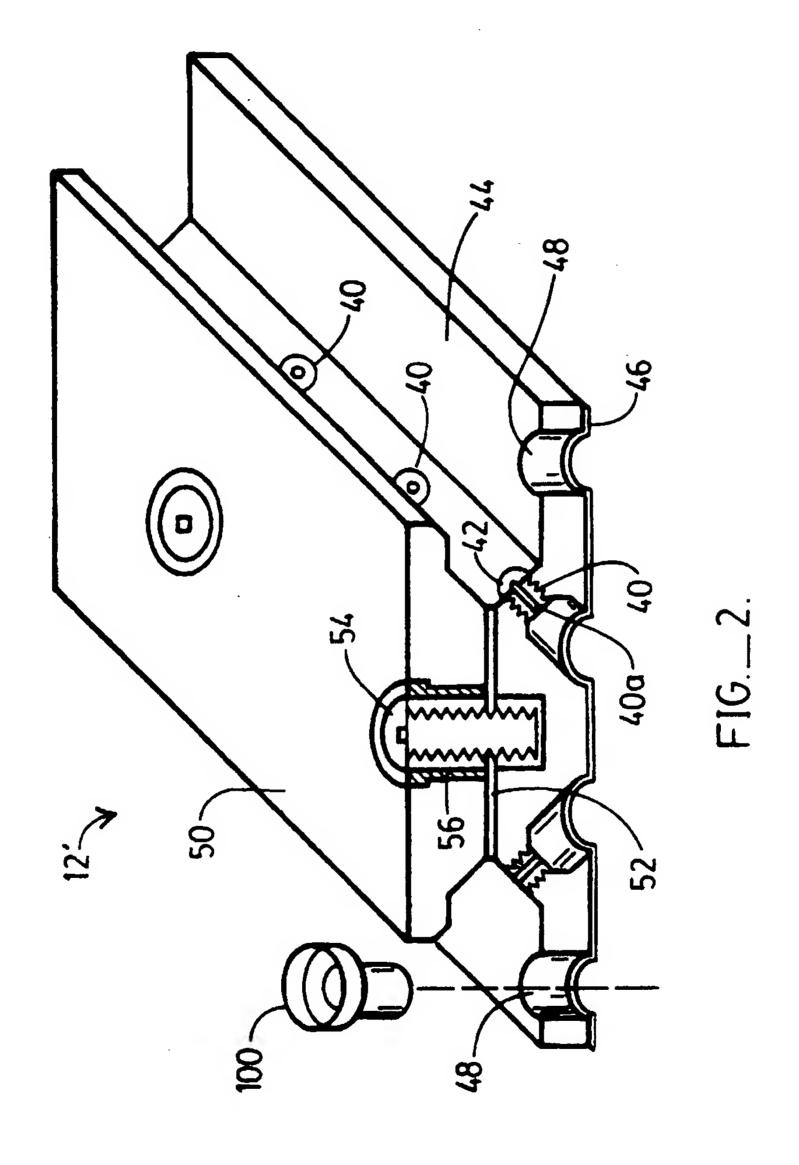


FIG.__1.



(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3: 06.05.1998 Builetin 1998/19

(51) Int Cl.6: H01J 37/32

(11)

- (43) Date of publication A2: 05.11.1997 Bulletin 1997/45
- (21) Application number: 97302893.9
- (22) Date of filing: 28.04.1997
- (84) Designated Contracting States:

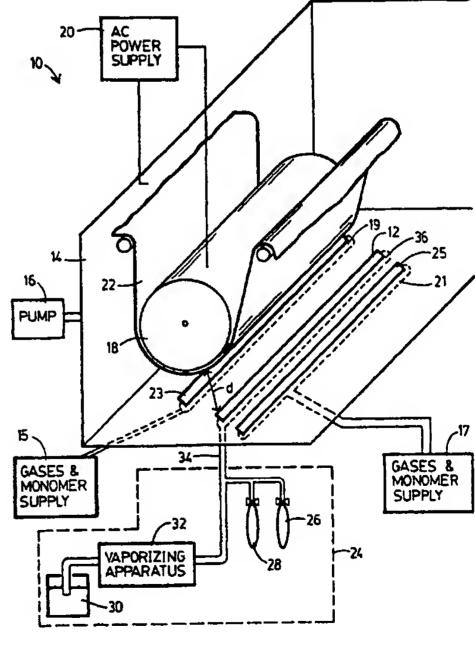
 BE CH DE DK FI FR GB IT LI NL SE
- (30) Priority: 01.05.1996 US 640460
- (71) Applicant: THE BOC GROUP, INC.
 Murray Hill, New Providence,
 New Jersey 07974-2082 (US)

- (72) Inventors:
 - Rietzel, James, G.
 Antoch, California 94509 (US)
 - Woolley, Christopher, P.
 Martinez, California 94553 (US)
- (74) Representative: Bousfield, Roger James et al The BOC Group plc Chertsey Road Windlesham Surrey GU20 6HJ (GB)
- (54) Plasma enhanced chemical vapour deposition processes and apparatus
- (57) A plasma treating apparatus comprising:

an evacuable chamber (14);

a power source (20) connected to two electrodes in the evacuable chamber (14) so that a plasma can be formed for the treatment of a substrate (22) when it is placed in the evacuable chamber (14);

a gas supply (17) supplying gases for the plasma to a gas injector (12), the gas injector (12) including gas ports (42) for allowing gases to enter the evacuable chamber(14), wherein the gas ports (42) include plugs (40) made of a dielectric material, the plugs having a centre hole (40a) through which the gases pass into the evacuable chamber (14), the plugs (40) fitted securely into the gas injector (12) so that gas does not leak around the sides of the plug (40) into the evacuable chamber (14).



F1G._1.



EUROPEAN SEARCH REPORT

Application Number

EP 97 30 2893

Category	Citation of document with indi		Relevant	CLASSIFICATION OF THE
	of relevant passag	es	to claim	APPLICATION (Int.Cl.6)
A	whole document		1,3,9	H01J37/32
A	US 4 512 283 A (BONI * figure 2 *	FIELD ET AL.)	6	
A	PATENT ABSTRACTS OF vol. 012, no. 168 (E-8 JP 62 278734 A (U-1987, * abstract *		1	
				TECHNICAL FIELDS
				SEARCHED (Int.Cl.6)
				H01J C23C
		•		
	The present search report has be	een drawn up for all claims		
<u> </u>	Place of search	Date of completion of the search	1-1	Examiner
	THE HAGUE	16 March 1998	Ca	postagno, E
X:pa Y:pa do: A:tec O:no	CATEGORY OF CITED DOCUMENTS rticularly relevant if taken alone rticularly relevant if combined with anoth- cument of the same category chnological background in-written disclosure ermediate document	L document cited	ocument, but pub ate in the application for other reasons	olished on, or n s